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^{27}Al and ^{29}Si NMR study of sol–gel derived aluminosilicates and sodium aluminosilicates

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Solid state ^{27}Al and ^{29}Si NMR was used to examine the structures of aluminosilicates and sodium aluminosilicates prepared by the sol–gel method from metal alkoxides. In contrast to the borosilicate system, where B–O–Si bonds are not formed until heat treatment above 150° C, Al–O–Si formation appears complete upon gelation. Aluminium occupies tetrahedral $[AlO_4]^-$ sites in the polymer network and octahedral $[Al(H_2O)_6]^{3+}$ (or similar) sites in the intersticies for charge balance. When sodium is added as a counter ion the octahedral aluminium is converted to tetrahedral aluminium in the oxide network. In gels of high aluminium content prepared from $(Bu^sO)_2Al–O–Si(OEt)_3$, some aluminium in five coordinate environments is also observed. All gels remain amorphous on heating to 800° C.

1. Introduction

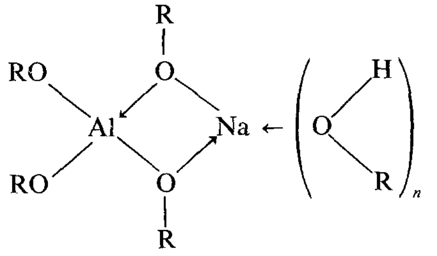
The sol–gel process using metal alkoxides is being extensively explored as a method for the preparation of homogeneous multicomponent glasses. In this context, such questions as homogeneity at the atomic level and structural differences between sol–gel and conventionally prepared materials are of great interest. Nuclear magnetic resonance (NMR) spectroscopy is a powerful technique for the study of multicomponent sol–gel systems. For example, we have recently shown using NMR that in the borosilicate system, B–O–Si bonds are not formed until heat treatment of the gels above 150° C [1, 2].

A number of workers have recently used ^{27}Al and ^{29}Si NMR to study various minerals and zeolites [3–8], the latter of which are aluminosilicate materials prepared by crystallizing gels derived from aqueous solution. The extensive data available on these materials should provide a good starting point for the interpretation of similar data on alkoxide-derived gels, which is the objective of the present study. Of particular interest is the environment of aluminium atoms in sol–gel derived materials. At what stage do the Al–O–Si bonds, required for homogeneity on the atomic scale, form? Aluminium can exist in oxide networks in 4, 5 or 6-coordinate environments. In minerals all of these coordinations may exist in the oxide framework [3, 4]. In zeolites however, it has been found that network aluminium exists only in the tetrahedral $[AlO_4]^-$ configuration, while octahedral aluminium is present only as a non-network species such as $[Al(H_2O)_6]^{3+}$ required for charge balance [5, 6]. If octahedral aluminium exists in gels as a network species $[AlO_6]^{3-}$, the addition of sodium as a counter ion should stabilize it. If on the other hand, 6-coordinate aluminium in gels is present as $[Al(H_2O)_6]^{3+}$ acting to balance the network charge, then the addition of Na^+ may free this octahedral aluminium to participate in Al–O–Si bonding in the network.

2. Experimental details

Aluminosilicate gels were prepard by two different methods, shown schematically in Fig. 1. All reactions were carried out under dry nitrogen on a Schlenk line. Glassware was oven-dried and assembled while hot. Isopropanol was dried and distilled before use. Water was distilled and de-ionized, methanol and ethanol were not dried. Tetraethylorthosilicate (TEOS) and 25 wt % sodium methoxide in methanol (Aldrich, Milwaukee, Wisconsin) and di-s-butoxyaluminoxytriethoxysilane (Petrarch Systems, Bristol, Pennsylvania) were used as-received.

Aluminosilicate gels containing sodium were prepared by a double alkoxide method shown schematically in Fig. 2. A sodium–aluminium double alkoxide of type I [7] was first prepared by reacting sodium methoxide with aluminium s-butoxide in a mixture of methanol and isopropanol. The double alkoxide, which remained soluble, was then added to partially hydrolysed TEOS. This method allowed the preparation of clear gels having Na : Al mole ratios of 0.25 to 10 without precipitation.



(I)

Sols were cast into capped glass vials for gelation. Vials were uncapped for drying at 40 and 150° C in an oven. Gels were heat treated to higher temperatures in porcelain crucibles in an electric furnace, and no

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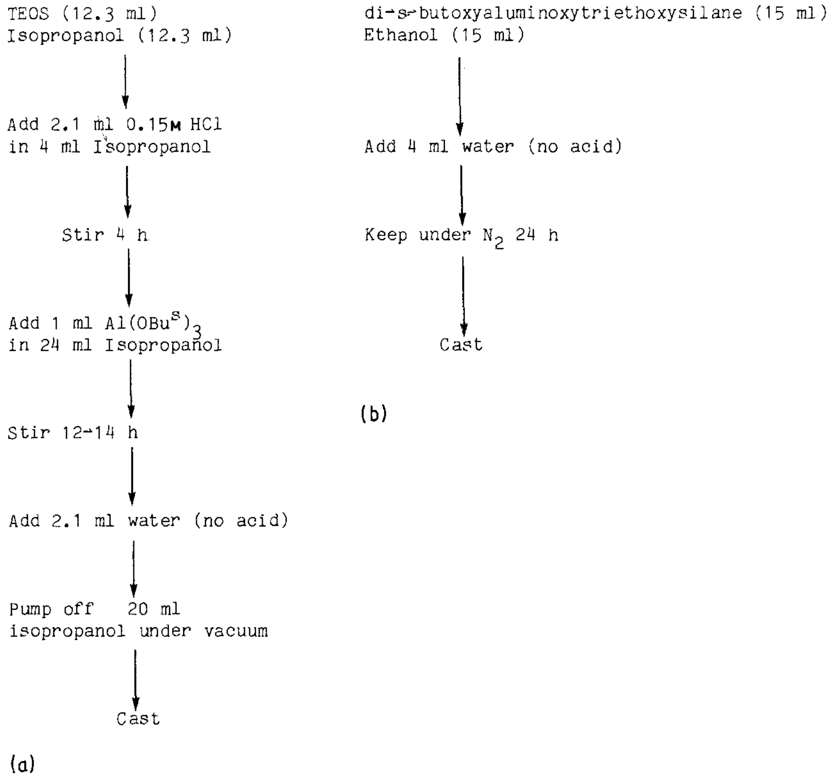

Figure 1 Methods used to prepare aluminosilicate gels without sodium: (a) using separate alkoxides, (b) using di-s-butoxyaluminoxytriethoxysilane.

vacuum or special atmospheres were applied during drying or heat treatment.

Natural abundance ^{29}Si NMR spectra were obtained at 59.6 MHz on a GN-300 (General Electric) spectrometer with Chemagnetics solids accessories. Magic angle spinning was performed at 3 kHz in 9.5 mm delrin spinners. Spectra were obtained both with cross-polarization (9 msec contact time) and without 150 sec delay interval), and strong proton decoupling was applied during acquisition. Chemical shifts are reported against an external sample of liquid TMS, with positive shifts to higher frequency.

^{27}Al NMR spectra were obtained at 78.2 MHz on the same spectrometer used for ^{29}Si spectra. The delay interval was 400 msec and strong proton decoupling was gated during acquisition. Chemical shifts are

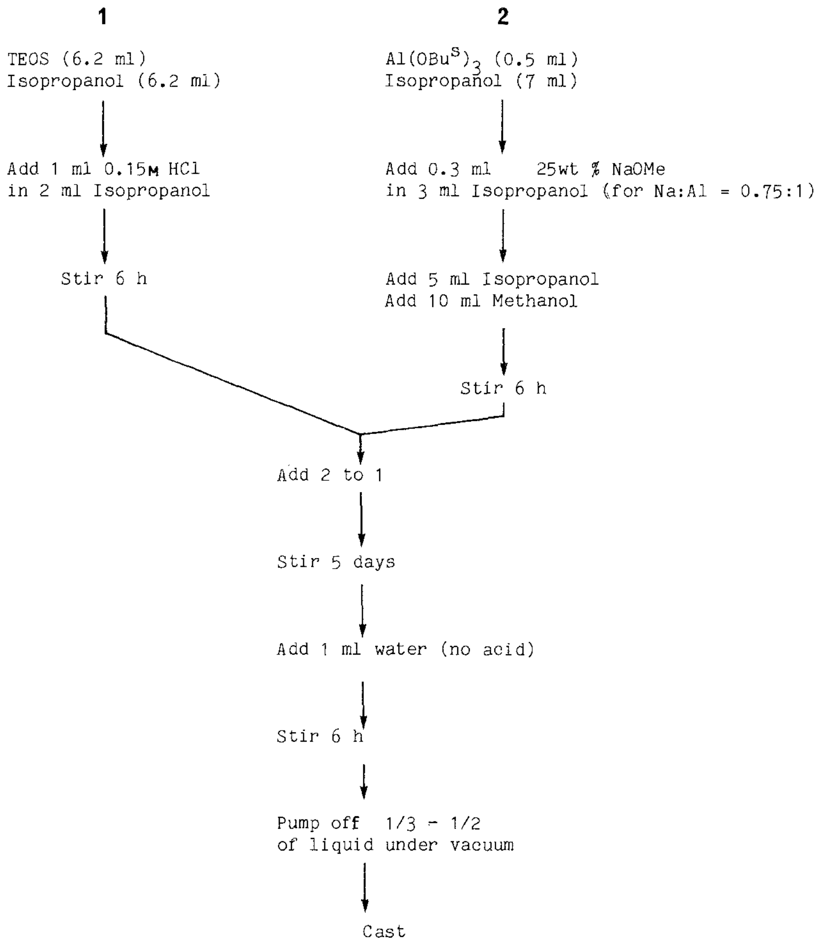

Figure 2 Double alkoxide method used to prepare aluminosilicate gels containing sodium.

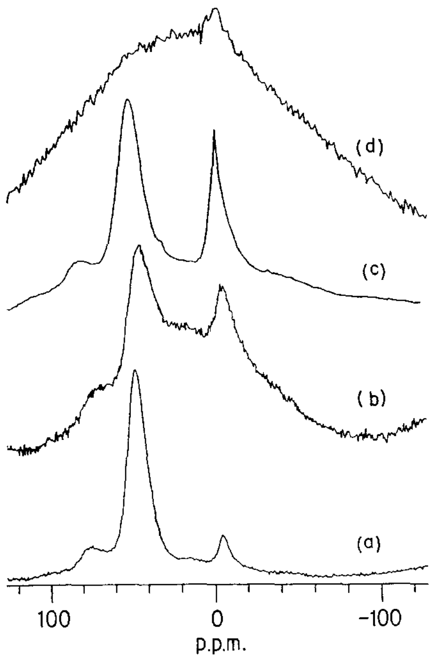

Figure 3 ^{27}Al MAS NMR spectra of the aluminosilicate gel of Fig. 1a at various stages of thermal treatment (a) 40° C, 6 h; (b) 150° C, 6 h; (c) 450° C, 2 h; (d) 800° C, 2 h.

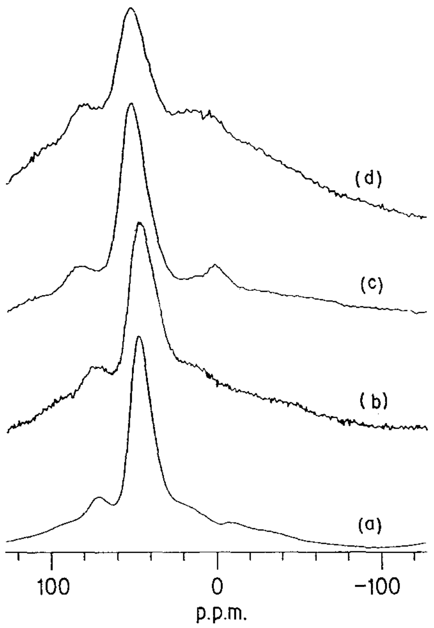

Figure 4 ^{27}Al MAS NMR spectra of a sodium aluminosilicate gel with Na : Al = 0.75 : 1 at various stages of thermal treatment. (a) 40° C, 6 h; (b) 150° C, 6 h; (c) 450° C, 2 h; (d) 800° C, 2 h.

given from an external sample of aqueous aluminium nitrate, with positive shifts to higher frequency.

3. Results and discussion

Fig. 3 shows the ^{27}Al spectrum of an aluminosilicate gel prepared from TEOS and aluminium s-butoxide by the procedure of Fig. 1a, after heat treatment to various temperatures. These spectra are similar to those observed by Aukett *et al.* for zeolite ZSM-5 [8]. The broader peak at 52 p.p.m. is due to aluminium atoms in tetrahedral $[AlO_4]^-$ environments, and the sharper resonance at 1 p.p.m. is from octahedrally coordinated aluminium. The small peak to the high-frequency side of the tetrahedral peak is a spinning sideband [9, 10]. The octahedral peak grows upon heating to 450° C, until at 800° C the spectrum becomes too broad to resolve. Fig. 4 gives the ^{27}Al spectra for a gel of the same composition, but containing sodium in the mole ratio 0.75 : 1 Na : Al. The octahedral peak is initially absent in this sample, and appears very weakly after heat treatment to $\geqslant 450°$ C. We observed the same behaviour for the entire range of Na : Al ratios (0.25 to 10) investigated. After heat treatment to 800° C the gels containing sodium still give resolved ^{27}Al spectra with tetrahedral aluminium as the principal component (Fig. 4d).

We interpret these results as follows. In aluminosilicate gels without sodium, tetrahedral $[AlO_4]^-$ groups exist in the oxide network which are charge balanced by octahedral aluminium cations ($[Al(H_2O)_6]^{3+}$ or similar). When Na^+ is added it acts as a counter ion, enabling more of the aluminium to become involved in $[AlO_4]^-$ network tetrahedra. This same behaviour was observed by Ione *et al.* [5] during removal of sodium from Na–Y zeolite. This material, which initially had only a tetrahedral aluminium peak, showed the emergence of an octahedral aluminium peak when the sodium was removed chemically. Fyfe *et al.* [11] also observed the charge balancing of tetrahedral framework aluminium by octahedral cationic aluminium species in zeolites by ^{27}Al NMR. The asymmetric lineshape of the octahedral peak in the spectra of Figs 3 and 4 may indicate the existance of more than one cationic aluminium species [8].

The ^{29}Si NMR spectra of the aluminosilicate and sodium aluminosilicate gels are shown in Figs 5 and 6 respectively. The spectra of gels heated to $\leqslant 450°$ C (Figs 5a to c and 6a to c) were obtained using ^{1}H–^{29}Si cross-polarization (CP) to enhance the signal to noise ratio, S/N. Spectra were also obtained without CP, and show no noticeable differences except decreased S/N. The spectra of gels heated to 800° C (Figs 5d and

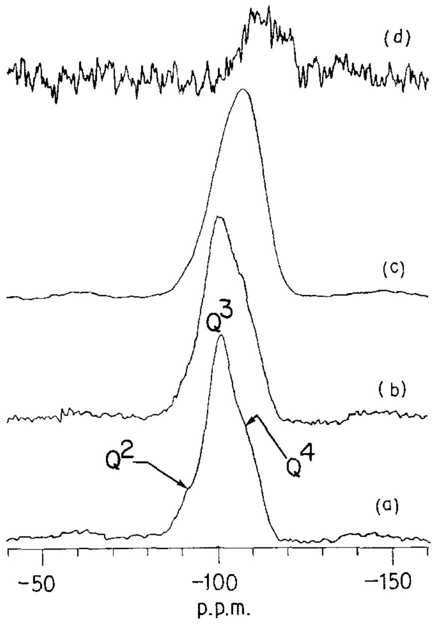

Figure 5 ^{29}Si MAS NMR spectra of the aluminosilicate gel of Fig. 1a at various stages of thermal treatment. (a to c), Cross-polarized spectra, (d) not cross-polarized (see text). (a) 40° C, 6 h; (b) 150° C. 6 h; (c) 450° C, 2 h; (d) 800° C 2 h.

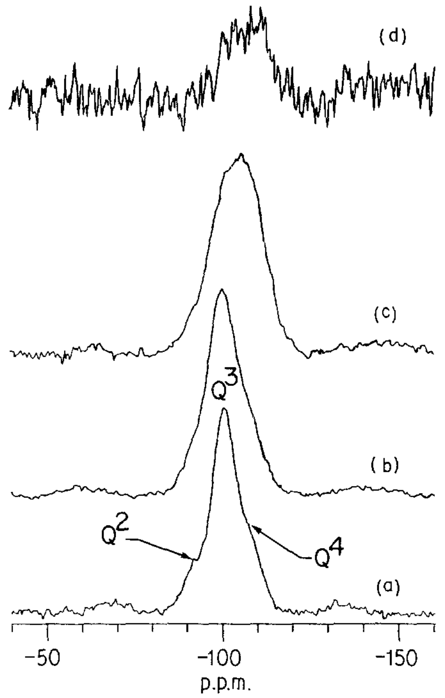

Figure 6 ^{29}Si MAS NMR spectra of a sodium aluminosilicate gel with Na : Al = 0.75 : 1 at various stages of thermal treatment. (a to c) cross-polarized spectra, (d) not cross-polarized (see text). (a) 40° C, 6 h;(b) 150° C, 6 h; (c) 450° C, 2 h; (d) 800° C, 2 h.

6d) were obtained without cross-polarization and have much poorer S/N than the CP spectra. In contrast to gels heated to $\leqslant 450°$ C, we were unable to attain any S/N enhancement for the gels heated to 800° C by cross-polarization (see later).

The very large linewidths observed in the ^{29}Si spectra are indicative of a broad distribution of environments in the second coordination sphere of silicon and the amorphous nature of these gels [12–15]. In contrast to borosilicate and pure silica gels, where the Q^2, Q^3 and Q^4 silicon sites are well-resolved in the ^{29}Si spectra of gels heated to $< 150°$ C [1, 16], the aluminosilicate gel exhibits severely decreased resolution, even in the initial gel (Fig. 5a). This same effect is observed in the initial amorphous gels prepared as zeolite precursors and has been atrributed to the wide range of chemical environments in the second coordination sphere of silicon caused by Al–O–Si bonding [12–14]. It appears that Al–O–Si bonds are already formed at the time of gelation. Unlike zeolite precursor gels, however, these alkoxide-derived gels remain amorphous and do not crystallize upon heat treatment.

The evolution of these spectra during heat treatment is indicative of increasing silicon condensation. The shoulder at −92 p.p.m. in Fig. 5a, due to silicon atoms in Q^2 sites, disappears, and the centre of the main resonance shifts from −101 p.p.m. (Q^3 silicon) to −107 p.p.m. (Q^4 silicon) upon thermal treatment to higher temperatures. This shift, however, lies toward the deshielded end of the normal Q^4 range, as would be expected for some of the silicons having aluminium in their second coordination sphere (Si–O–Al) [17]. The same behaviour is observed in the ^{29}Si NMR spectra of gels containing sodium (Fig. 6), except that in gels containing larger amounts of sodium ($\geqslant 5:1$ Na : Al) the centre of the Q^4 resonance is shifted a little further downfield to −102 p.p.m., as would be expected if more aluminium was involved in Al–O–Si bonding in these gels. When Na$^+$ is added, cationic aluminium which is no longer required for charge balance is free to become tetrahedral $[AlO_4]^-$ in the silica network.

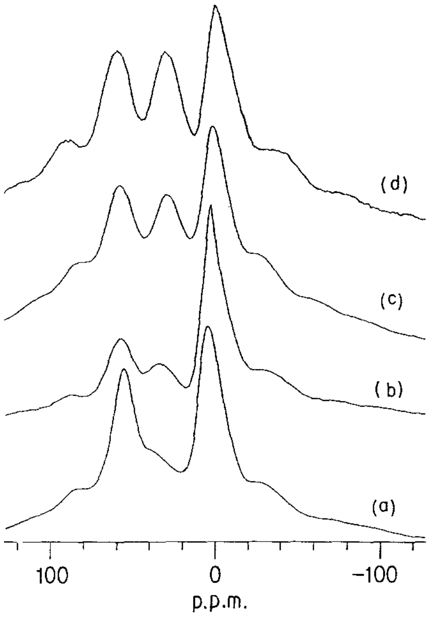

Figure 7 ^{27}Al MAS NMR spectra of the aluminosilicate gel of Fig. 1b at various stage of thermal treatment (a) 40° C, 6 h; (b) 150° C, 6 h; (c) 450° C, 2 h; (d) 800° C, 2 h.

The inability to cross-polarize gels heated to 800° C indicates that directly bonded silanol ($\equiv$Si–OH) groups no longer play an important part in the structure of these gels [15]. In studying the ^{29}Si spectra of pentasil type zeolites and their precursor gels, Debras *et al.* [6] found no detectable silanol in their calcined samples, and found a significant amount of silanol groups only in gels of low sodium or aluminium content. Englehardt *et al.* [6, 18] observed no enhancement in S/N for ^{29}Si CP spectra of sodium-containing zeolite A. The paucity of silanol groups may be due to the loss of OH as water upon heating to 800° C, facilitated by the presence of Na$^+$ or cationic aluminium species to fill the $\equiv SiO^-$ surface vacancies in these samples, or possibly the elimination of silanol groups by condensation [19]. In the case of charge balance at $\equiv SiO^-$ sites by cationic aluminium species, these species would almost certainly contain protons (e.g. $[Al(H_2O)_6]^{3+}$), but their distance from silicon or their mobility may preclude effective cross polarization.

The ^{27}Al NMR spectrum of an aluminosilicate gel is made from di-s-butoxyaluminoxytriethoxysilane, $(Bu^sO)_2Al–O–Si(OEt)_3$, using the procedure of Fig. 1b is shown in Fig. 7. In addition to the tetrahedral and octahedral aluminium peaks at 52 and 1 p.p.m., respectively, this gel also gives a peak at 29 p.p.m. This peak has been observed in barium aluminium glycolate and in the mineral andalusite by Alemany and Kirker [4], and in anodically formed amorphous alumina films by Dupree *et al.* [20], and has been assigned to 5-coordinate (AlO_5) aluminium. The relative intensity of this five-coordinate peak increases during thermal treatment. The ^{29}Si spectrum of this sample is given in

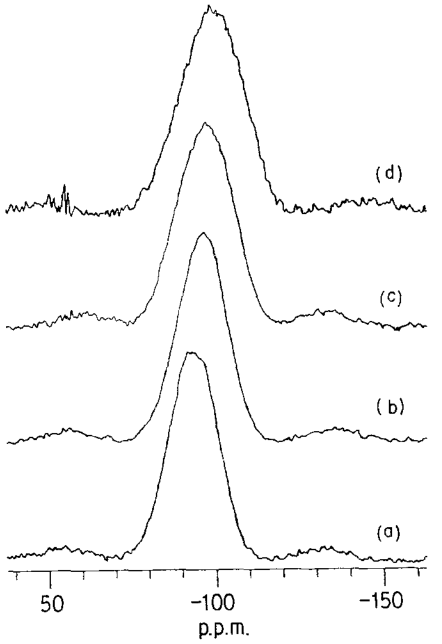

Figure 8 ^{29}Si MAS NMR spectra (cross-polarized) of the aluminosilicate gel of Fig. 1b at various stage of thermal treatment (a) 40° C, 6 h; (b) 150° C, 6 h; (c) 450° C, 2 h; (d) 800° C, 2 h.

Fig. 8. The ^{29}Si resonance shows only one broad peak, with no resolution of Q^2, Q^3 and Q^4 groups at all, even in the initial gel (Fig. 8a). These peaks have half width of 1000 Hz, as opposed to 850 Hz for the spectra of Figs 5 and 6. The equally spaced small peaks flanking the ^{29}Si resonance are spinning sidebands. All spectra in Fig. 8, including the gel heated to 800° C, were obtained with ^{1}H–^{29}Si cross-polarization, indicating that this gel contains protons close to silicon (e.g. silanol groups) even after heating to 800° C. The centre of the peak moves from -94.0 to -99.4 p.p.m. as the gel is heated from 40 to 800° C. This sample contains much more aluminium than the other studied, and has a 1 : 1 Si : Al mole ratio. The ^{29}Si chemical shift is in the range expected for Si(2Al) rather than the -84 p.p.m. neighbourhood of Si(4Al) [17]. This indicates that a substantial portion of the aluminium in this gel is not part of the oxide network, but is outside of it, perhaps acting to balance the network charge. For a 1 : 1 ratio of Si : Al, the expected silicon environment is Si(4Al) if all the aluminium is part of the oxide network, unless the Lowenstein rule (which prohibits Al–O–Al bonds) is violated.

4. Conclusion

Aluminosilicate gels have been prepared from alkoxides by two approaches: (a) reaction of TEOS with aluminium s-butoxide, and (b) hydrolysis of $(Bu^sO)Al–O–Si(OEt)_3$. Sodium aluminosilicate gels were prepared by first reacting sodium methoxide with aluminium s-butoxide to make a soluble double alkoxide, then adding this double alkoxide to partially hydrolysed TEOS. The resulting gels were studied by ^{27}Al and ^{29}Si MAS NMR at various stages of thermal treatment to 800° C. All gels studied show evidence of Al–O–Si units upon gelation. Aluminosilicate gels prepared from separate alkoxides contain tetrahedral aluminium in the oxide framework, which is charge balanced by octahedral cationic aluminium moieties. The addition of sodium to these gels frees the cationic aluminium, which then becomes tetrahedral aluminium in the oxide network. Aluminosilicate gels made by hydrolysing $(Bu^sO)_2Al–O–Si(OEt)_2$ contain aluminium in tetrahedral, octahedral and five-coordinate environments.

Acknowledgements

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